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(54) **Weather-resistant, PVC-free Flat Materials Based on Textiles**

(57) The invention relates to a flat material based on textiles, comprising (a) a flat textile structure and (b) at least one impregnation of the flat textile structure or one coating applied to the textile structure, characterized by the fact that the coating or impregnation material contains a binder that has at least 30 wt.%, referred to the total amount of binder, of an acrylate/VeoVa copolymer. The impregnation or coating can additionally contain a flame retardant. The material according to the invention is very resistant to environmental effects and mechanical stress and is suitable, for example, for use as a tunnel covering, swimming pool cover or for truck tarpaulins.

Description

[0001] The present invention relates to coated textile materials that are suitable, among other things, for applications outdoors or in wet rooms, and are also durable under extreme environmental conditions.

[0002] Flat materials based on textiles that can resist extreme environmental stresses, for example, high humidity, rain and spray water, temperature fluctuations, intense solar radiation and/or frequent treatment with cleaning agents, are ordinarily coated with PVC. The properties of such materials are very good. However, the use of PVC is objectionable and should be avoided as much as possible. Its production and application as a coating material for textiles are associated with serious environmental burdens, as is disposal of the material. Toxic gases are also created in a fire (for example, hydrogen chloride).

[0003] The same applies for rubber materials, as well as materials coated with acrylates or polyurethanes on a solvent basis. Their production and application to the corresponding textile materials is associated with severe environmental burdens, and the excellent properties of PVC, with respect to loading capability of the textile material, are also not achieved.

[0004] Coatings having an aqueous base are much more environmentally friendly; however, they do not meet the aforementioned requirements.

[0005] PVC is a very inexpensive material. For this reason and because of its favorable properties in textile coatings, it is used in high percentages.

[0006] The task of the present invention is to furnish coated or impregnated textile materials that possess similarly good properties to PVC with respect to their chemical and mechanical cleaning stability (for example, relative to high-pressure cleaners or brush cleaners), water tightness and weather stability, but also other environmental effects, but can be processed in an environmentally friendly fashion, release no toxic gases in a fire and can be produced cost effectively.

[0007] It was surprisingly found that such textile materials meet the mentioned requirements if the binder or at least one of the coatings applied to it, or the impregnation, has a significant ratio of acrylate/VeoVa copolymer. This ratio is at least 30 wt.%, preferably at least 50 wt.%, with greater preference 70-100 wt.%, and especially 85-100 wt.%, referred to the total amount of binder.

[0008] Acrylate/VeoVa copolymers are known. VeoVa in this name stands for vinyl ester of tertiary carboxylic acids (for example, versatic acids). VeoVa's have long been used for copolymerization with vinyl acetate, for example for dispersion paints, plasters or concrete additives. Copolymers of VeoVa's with acrylates are commercially available, and they are marketed mostly for production of plasters and paints.

[0009] The invention is applicable to all textile materials that are to be provided with binder-containing coatings or impregnations. All flat textile materials, regardless of the method in which their fibers are joined to each other, can be coated or impregnated, for example, woven, non-woven, knit products, etc. The material prescribed for the flat textile can also be freely chosen as a function of the prescribed use. In this case, if necessary, the mechanical stress of the fibers is to be considered. Depending on the area of application of the coated textile materials according to the invention, the choice of the support materials is made appropriately. For example, support materials based on synthetic fibers (polyester, polyamide, polyacrylonitrile or other such fibers) can be used for applications in outdoor sun protection, outdoor sight protection, landfill covers, room dividers for wet rooms and the like. If the materials according to the invention are prescribed for applications connected with high mechanical loads, high-strength polyester filaments, glass filaments or para-aramid fibers can be used as support materials. Support materials from non-combustible or poorly flammable materials (for example, glass fibers, aramid fibers, melamine resin fibers, ceramic fibers, etc., or fibers that are fire-proofed by additional finishing) will also be considered, in particular, by one skilled in the art, if an application in surroundings that are to be protected from fire or are vulnerable to fire is prescribed, for example, when the textile materials according to the invention are prescribed for escape route boundaries or wall cladding, especially in tunnel wall cladding, outdoor exhibits, scaffold construction or the like.

[0010] Depending on the application, the textile substrates can be provided with the coating according to the invention on one or both sides. This coating can be present as a single coating or several coatings. As an alternative (optionally also in addition), they can be provided with an impregnation, which is applied by impregnation of the textile material or another ordinary impregnation technique.

[0011] The coating/impregnation according to the invention can consist essentially or exclusively of binders. It can also contain other ordinary binders, in addition to the

acrylate/VeoVa copolymer, for example, polymers based on acrylic acid esters, polyvinyl alcohol, polyurethane, latices or highly crosslinkable resins, like melamine resin, which are preferably halogen-free, and which also preferably are crosslinkable, so that they can be fixed accordingly. However, it is particularly favorable if the binder consists mostly or, with particular preference, exclusively or almost exclusively of acrylate/VeoVa copolymer. The binder is used in the form of a solution, emulsion, dispersion or suspension, with which the textile substrate is coated or impregnated. If the paste is too fluid, the viscosity can be adjusted with a thickener (for example, an acrylic acid ester). If necessary, appropriate crosslinking catalysts are added to the paste.

[0012] Instead of this, the coating/impregnation according to the invention can also contain other ingredients that influence its properties. In an important embodiment according to the invention, a coated or impregnated material is provided, which has fire-retardant properties and is suitable, for example, for the lining of tunnels. In this embodiment of the invention, the coating/impregnation, in addition to the binder and optionally additional substances, mostly contains a strongly fire-retardant material, like expanded graphite and/or a phosphorous-containing material, for example, polyammonium phosphate. In the presence of a solid fire-retardant material, like expanded graphite, coating of the textile substrates is preferable over impregnation. A fire-retardant material can be added to the coating mixture in appropriate form, for example in powder, granulate or flake form, if a solid material is involved. The amount ratio of binder to fire retardant, for example, and especially to expanded graphite, can be freely chosen in appropriate fashion, in which it is naturally favorable to provide a high percentage of flame retardant, for example 10-80 wt.%, referred to all the ingredients of the coating material. The upper limit is generally dictated by the mechanical properties of the cured coating: For the case of a solid flame retardant, like expanded graphite, it must be ensured that sufficient binder is present, in order to bind the flame retardant into the layer in mechanically stable fashion. The lower limit is dictated by the flame-retardant properties of the obtained material: The coating should contain a sufficient amount of flame retardant, so that its flame-retardant effect, and optionally the insulation effect achieved by the volume increase, is fully considered. In the case of expanded graphite, this is generally at least about 30 g expanded graphite per square meter of textile material, preferably about 50 to 500 g/m^2. With reference to the content of VeoVa/acrylate copolymer in the binder, what was stated in the previous paragraph applies.

[0013] It is particularly preferred, in the case of a light-absorbing flame retardant, like expanded graphite, that the flame-retardant coating just described also contains a white pigment, for example, titanium dioxide, alabaster brilliant white, kaolin or a similar material. As an alternative or in addition, a white pigment-containing layer that can also contain a binder can also be applied to the already applied coating material before or after curing. If the white pigment is incorporated into the coating mixture containing the expanded graphite, it is favorable to provide 3-10 wt.% white pigment, referred to the total weight of the paste. If the white pigment is applied as an additional coating to the expanded graphite coating, it is sufficient to apply only a limited amount of about 2-10 g/m^2. The white pigment can be used for this purpose as a suspension in an appropriate suspension agent or adulterant and added in an amount of about 1:4 of a suspension or dispersion of an appropriate binder or crosslinking agent, especially consisting or mostly consisting of VeoVa/acrylate copolymer, as stated above for the coating mixture containing expanded graphite.

[0014] The coating or impregnation material can optionally contain additional ingredients, like those ordinarily used, for example, dyes or pigments, thickeners, buffers or agents for setting a specific pH value, stabilizers, fillers and the like.

[0015] In order to make the coated/impregnated textile materials according to the invention particularly stable relative to chemical, and especially strong mechanical cleaning (for example, with high-pressure cleaners or brush cleaners, which are often used, for example, in the case of truck tarpaulins or tunnel coverings), their surface can be appropriately modified. This can occur, for example, by hydrophobing of the surface and/or by improvement of its mechanical strength values. In order to make the surface hydrophobic, fluorocarbon resins, paraffin waxes, silicones or polytetrafluoroethylene dispersions can be incorporated into the coating/impregnation mixture according to the invention, if this is prescribed alone or as the only or uppermost layer. Additional crosslinking with an additional crosslinking agent can also improve the mechanical stability and possibly make the coating more hydrophobic. As an alternative, the uppermost layer can be impregnated with an appropriate hydrophobing agent, or a cover layer ("topcoat") can be applied, which is particularly scratch-resistant. Other possibilities include coating or impregnation with materials that produce specific surface structures with extremely good dirt-repellent properties (for example, "nanocoatings" with a "lotus effect") or plasma treatment with hydrophobing gases.

[0016] The coating hardness is easily controlled by the mixing ratio of hard and soft polymers. One skilled in the art will select polymers with appropriate glass transition points for the corresponding application. Different variants of acrylate/VeoVa copolymers with different degrees of hardness are commercially available.

[0017] If a coating on a textile material is prescribed according to the invention, this is preferably applied in the form of a paste or foam to the textile material. Application can occur by doctor coating, for example roll coating, spreading or any other method, the choice of which is guided, among other things, by the viscosity of the coating material. The appropriate amounts can be easily determined by one skilled in the art, and a wet coating of 25-400 g/m^2 is favorable. Excess solvent or dispersant is then optionally removed, for example by drying, and the coated paste is calendered or strengthened/cured in some other way, depending on the type of components present, for example, by heat or light; self-curing, crosslinkable components can also be present. It can also prove useful to apply the coating material in more than merely one working step to the textile material and after each working step, or only after application of the entire coating material, to provide a strengthening step, for example, after drying.

[0018] If the coating formed in this way is to be covered with one or more layers (for example, a white pigment paste or a topcoat), the required drying and curing steps can also be carried out only after the application of several or even all layers.

[0019] The invention will be further explained below by means of examples.

Example 1:

[0020] A glass fabric from EC-9 68tex with a base weight of 205 g/m^2 was coated on both sides with the following formula:

- Enorex AVE 191 (copolymer from acrylate/VeoVa, from Collano Ebnöther AG, Switzerland) 60 parts
- Enorex H 276 AV
  (weakly carboxylated VeoVa/acrylate copolymer from Collano Ebnöther AG, Switzerland) 20 parts

- Dicrylan FLN
  (ammonium-alkylamine stearate from Ciba) 16 parts
- Pigment dye 4 parts

[0021] The charge was foamed with a Hansa mixer (foam density 260 g/L) and applied on a Mageb coating unit according to the roll-coating method with a gap height of 0.85 mm. A total base weight of 370 g/m^2 at a thickness of 0.3 mm resulted from this. The coated fabric was immediately calendered after drying (80-140°C) while hot (140°C roll temperature) (linear pressure: 180 N/mm).

[0022] A fabric coated on both sides with very good scratch resistance is obtained and a film-like, PVC-like surface, which can be wound without blockage. The coating is resistant to water (cold and hot), even during several months of storage. It is also stable relative to dilute alkalis and oils and conditionally stable relative to acetic acid (60%), gasoline and solvents (tested by 24-hour insertion in the respective medium). Water vapor stability is also present. The stability is comparable, with respect to most of the aforementioned media, to that of PVC-coated fabric, however the resistance of the material according to example 1 to acetone is much better.

Example 2

[0023] A polyester fabric from OE yarn Nm 34 with a base weight of 110 g/m^2 was coated on one side with the following formula:

- Enorex AVE 191
  (copolymer from acrylate/VeoVa, from Collano Ebnöther AG, Switzerland) 60 parts
- Pyrovatim SB
  (flame-retardant polyammonium phosphate, with fractions of melamine/formaldehyde condensates, Ciba) 12 parts
- Appretan 9213
  (acrylate copolymer dispersion, self-crosslinking, Clariant, Frankfurt/M) 18 parts
- Ammonia water 25% 1.6 parts
- TC thickener SD
  (acrylate thickener, Texticolor AG, Sevelen/Switzerland) 2.4 parts

[0024] The charge, with a viscosity of 1.7-1.8 Pas, was coated 3 times on one side on a Brückner-stretching frame according to the air coating process. The coating was dried and crosslinked for 90 seconds at 150°C. The coating weight is 150 g/m^2 dried.

[0025] A poorly flammable fabric coated on one side is obtained. The coating is mechanically very loadable, especially relative to abrasion, and very stable relative to cleaning with high-pressure cleaners. The flame retardant also does not rinse off the coating composite after repeated cleaning cycles.

Example 3

[0026] A fabric with a base weight of 225 g/m^2 from Nm 40/2 Basofil (melamine resin fiber from BASF) and Technora or Kevlar (para-aramid fiber; Kevlar is a trademark of DuPont) in a ratio of 60:40 was coated on one side with 27.5 warp threads per cm and 15 weft threads per cm in a 2/1 twill weave with a paste consisting of

– Kappaflamm T2/163 (paste with 55% expanded graphite from Kapp-Chemie)	50 parts by weight
– Enorex AVE 191	40 parts by weight
– Pyrovatim SB	10 parts by weight
– Kronos RN 43 (titanium dioxide, Kronos)	7 parts by weight
– Baysilone oil (silicone oil, Bayer company)	1 part by weight
– Ammonia water 25%	to pH 10
– TC thickener	to a viscosity of 1.9 Pas/s

[0027] The coating weight was 300 g/m^2. Impregnation then occurred with 30 g/L Oleophobol SD (fluorocarbon resin from Ciba Specialty Chemistry). The coating and impregnation were then crosslinked at 160°C.

[0028] A product is obtained with good flexibility with a gray-white coating side. In comparison with an expanded graphite coating without white pigment, the following optical measured values were obtained:

	With white pigment	Without white pigment
Absorption	45%	90%
Reflection	55%	10%

[0029] The visible wave spectrum from 400 to 700 nm was measured.

[0030] A sample of the material was soiled and cleaned with a high-pressure cleaner. After a relatively short cleaning time, a very good cleaning result was obtained; the coating remained undamaged.

[0031] To test the intumescence behavior, the material was exposed to the flame of a Bunsen burner. In the area of flame exposure, a volume increase of up to 180% occurred. A stable, expanded foam was formed with good insulation properties. The fabric showed no melt drop formation. The Basofil fraction produced a stable carbon framework.

Claims

1. Flat material based on textiles, comprising

   (a) a flat textile and

   (b) at least one impregnation of the flat textile or a coating applied to the flat textile,

   characterized by the fact that the coating or impregnation material contains a binder, having a fraction of at least 30 wt.%, referred to the total amount of binder, of an acrylate/VeoVa copolymer

2. Flat material according to Claim 1, **characterized by the fact that** the percentage of acrylate/VeoVa copolymer is at least 50 wt.%., more preferably at least 70 wt.%, and especially in the range from 80-95 wt.%.

3. Flat material according to Claim 1 or 2, **characterized by the fact that** the textile fabric is a non-woven material, a woven fiber material or a knitted fiber material.

4. Flat material according to one of the preceding claims, **characterized by the fact that** the material of the flat textile consists mostly or exclusively of synthetic fibers, especially those from polyester, polyamide or polyacrylonitrile or their mixtures, polyester filaments, glass filaments or para-aramid fibers, which optionally are or were made poorly flammable, glass fibers, aramide fibers, melamine resin fibers, ceramic fibers or Kevlar fibers, or mixtures of the aforementioned fibers or filaments or includes them.

5. Flat material according to one of the preceding claims, **characterized by the fact that** impregnation of the flat textile material or the coating applied to the flat textile material consists exclusively or mostly of binder.

6. Flat material according to one of the Claims 1 to 4, **characterized by the fact that** the impregnation of the flat textile material or the coating applied to the flat textile material also contains a flame-retardant material.

7. Flat material according to Claim 6, **characterized by the fact that** the flat textile material has a coating applied to it, and that the flame retardant is a phosphorus-containing material or expanded graphite.

8. Flat material according to Claim 7, **characterized by the fact that** the coating applied to the flat textile material contains about 20 to 70 wt.% binder and about 20 to 80 wt.% flame retardant.

9. Flat material according to Claim 7 or 8, **characterized by the fact that** the coating applied to the flat textile material also contains a white pigment.

10. Flat material according to one of the Claims 1 to 8, **characterized by the fact that** the coating applied to the flat textile material also contains a dye or dye pigment.

11. Use of a flat material according to one of the preceding claims as outdoor sun protection, outdoor visual protection, landfill cover, room divider for wet rooms, truck tarpaulin material, storage vessel material, tent material, swimming pool cover, life jacket material, material for escape route boundaries, wall cladding, especially for tunnel walls, or material in outdoor fair construction or scaffold construction, or as a component of the aforementioned materials.

RELEVANT DOCUMENTS

Category	Citation of document with indication, if applicable, of the relevant passages	Relates to Claim	CLASSIFICATION OF APPLICATION (Int. Cl. 7)
X	EP 0 874 871 B (WACKER CHEMIE GMBH) 4 November 1998 (1998-11-04) * Page 3, line 1 – line 23 * * Page 5, line 48 – line 52 * ---	1, 2	D06M15/263 C09D133/00 D06N3/04 C08F218/10
A	DE 197 33 133 A (WACKER CHEMIE GMBH) 4 February 1999 (1999-02-04) * The entire document * ---		
A	EP 1 106 724 A (WACKER POLYMER SYSTEMS GMBH &) 13 June 2001 (2001-06-13) * The entire document * ---		
A	WO 01 85465 A (BAMBERGER KALIKO GMBH; KLENNER PETER (DE); FUESSMANN KLAUS (DE); H) 15 November 2001 (2001-11-15) * The entire document * ---	1-11	
			SUBJECT AREAS SEARCHED (Int. Cl.[7]) D06M C09D C08F D06N

The present search report was prepared for all patent claims

Search site	Date search completed	Examiner
MUNICH	28 March 2003	Koegler – Hoffmann, S

CATEGORY OF CITED DOCUMENTS
X: of particular interest of itself
Y: of particular significance in association with another publication of the same category
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E: earlier document but published on or after the filing date
D: document cited in the application
L: document cited for other reasons
.....
&: supporting document that is member of the same patent family

ADDENDUM TO EUROPEAN SEARCH REPORT

CONCERNING EUROPEAN PATENT APPLICATION NO. EP 02 02 3481

The members of the patent families of the patent documents listed in the aforementioned European Search Report are stated in this addendum.

Information concerning family members corresponds to the status of the file of the European Patent Office on 03-28-2003

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Patent document cited in Search Report	Date of publication	Member(s) of patent family		Date of publication
EP 0874871 B	11-04-1998	DE	19601699 A1	07-24-1997
		AT	184296 T	09-15-1999
		CN	1208427 A, B	02-17-1999
		CZ	9802265 A3	10-14-1998
		DE	59700412 D1	10-14-1999
		WO	9726295 A1	07-24-1997
		EP	0874871 A1	11-04-1998
		ES	2138441 T3	01-01-2000
		JP	11503790 T	03-30-1999
		KR	275289 B1	12-15-2000
		PL	327856 A1	01-04-1999
		TW	467939 B	12-11-2001
		US	6242512 B1	06-05-2001
DE 19733133 A	02-04-1999	DE	19733133 A1	02-04-1999
		BR	9803726 A	05-16-2000
		CN	1208062 A	02-17-1999
		CZ	9802425 A3	02-17-1999
		DE	59800523 D1	04-19-2001
		EP	0894888 A1	02-03-1999
		ES	2156422 T3	06-16-2001
		JP	2994341 B2	12-27-1999
		JP	11172573 A	06-29-1999
		PL	327765 A1	02-01-1999
		RU	2149934 C1	05-27-2000
		TR	9801480 A2	08-21-2001
		US	5977244 A	11-02-1999
EP 1106724 A	06-13-2001	DE	19959415 A1	06-21-2001
		EP	1106724 A1	06-13-2001
		US	6472462 B1	10-29-2002
WO 0185465 A	11-15-2001	DE	10022471 A1	12-06-2001
		WO	0185465 A1	11-15-2001
		EP	1282525 A1	02-12-2003

For further details on this attachment : see Official Gazette of the European Patent Office, No. 12/82